

ROLE OF ALKALI METALS IN REDUCTION OF CARBON MONOXIDE IN MAINSTREAM SMOKE

Kazuyo Kaneki, Masao Matsukura and Yoshiaki Ishizuka
Tobacco Science Research Laboratory, Japan Tobacco Inc.,
6-2 Umegaoka, Midori-ku, Yokohama 227, Japan

SUMMARY

The formation rate of CO in mainstream smoke has been reported to be dependent on the potassium content in tobacco. This work was undertaken to elucidate the role of alkali metals in CO reduction. CO in cigarette smoke has been shown to be produced by three processes; thermal decomposition of the tobacco constituents, combustion of the tobacco constituents, or carbonaceous reduction of CO₂. In this paper, the contribution of alkali metals to each process of CO formation is discussed.

The DSC curve of tobacco char in air is made up of 2 peaks. In the case of the carbonaceous residue of tobacco treated with alkali metal salts, the first peak of the DSC curve, which is attributable to the oxidation of the more reactive portion of char, disappeared and the surface area of char decreased. However, the DSC curves obtained from a mixture of untreated tobacco char and alkali metal salts were not influenced by the amount of the salts. Accordingly, it is considered that alkali metal salts caused a more stable char to form during the decomposition process of tobacco. Also, the amount of oxygen consumed during the puff decreased, and the maximum temperature of the solid phase of the burning cone during the puff was lowered when alkali metals were added to the cigarette.

Consequently, the amount of CO formed in the combustion process was reduced by alkali metal salts. Moreover, the temperature of the burning cone was lowered, and the CO formed from carbonaceous reduction decreased.

INTRODUCTION

Decreasing the level of CO in mainstream smoke is important in cigarette manufacture. The formation rate of CO has been reported to be dependent mainly on the potassium content of tobacco (1,2). CO in cigarette smoke has been shown to be produced by three processes; namely, thermal decomposition of tobacco constituents, combustion of tobacco constituents, and carbonaceous reduction of CO₂. Each process produces about one third of the total quantity of CO formed in mainstream smoke (3). In this paper, the contribution of alkali metals to CO formation from each process is discussed.

In a previous paper (1), we discussed the idea that the temperature of the burning zone fell with the increase in potassium content of tobacco shreds, resulting in the decrease of CO formation via CO₂. However, alkali metal salts are used as accelerating catalysts for gasification of carbon black and coal, that is as accelerating catalysts for carbonaceous reduction of CO₂, and many studies on this mechanism have appeared (4). Therefore, we now

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believe that alkali metals are not directly related with the carbonaceous reduction of CO₂ in cigarettes.

EXPERIMENTAL

Unblended non-filter cigarettes were made from the cutter of Bright tobacco cultivars. The width of the cut shreds was 0.8 mm. Aqueous solutions of potassium malate and sodium malate were sprayed onto the shreds. The potassium and sodium contents added to the shreds was measured using Zeeman effect atomic absorption spectro-photometer (HITACHI type 6100). The length and circumference of the cigarettes were 70 mm and 25 mm, respectively. Cigarette paper with a permeability of 10 ml/cm²/min/100 mmw.g. was used. After conditioning at 22°C, 60% R.H., each sample was selected by weight to keep the fractional volume of the cigarettes constant (0.31 or 0.32). Cigarettes were smoked on a smoking machine under standard smoking conditions. The concentration of CO in the mainstream smoke was measured by a non-dispersive infra-red analyzer, and the concentration of O₂ was measured by an oxygen meter (IIJIMA Type RO-101).

Thermogravimetry was carried out using a TGS-1 Thermo-balance (Perkin-Elmer). Powdered tobacco with and without the additives was heated at a rate of 20°C/min under a flow of air or nitrogen (200 ml/min). The additives were potassium malate and sodium malate. In order to investigate the effect of alkali metals on the oxidation of tobacco char, tobacco chars were prepared by the method described by Muramatsu *et al.* (5). Tobacco shreds were heated in an electric furnace to 550°C at a constant heating rate of 20°C/min and then maintained at this temperature for 2 hours under a flow of nitrogen. DSC measurements of the following 2 samples were carried out in air atmosphere using DSC-41M (Shimadzu).

Sample A: Mixture of untreated tobacco char and K₂CO₃

Sample B: Char made from tobacco treated with potassium malate

The surface area of chars of Sample B was measured with the BET gas adsorption technique using nitrogen as the adsorbate gas. The equipment used was a Belsorp 28 (NIHON BELL). Before the measurement, sample chars were dried for 16 hours at 150°C under vacuum.

Ash samples were obtained from cigarettes which had been smoked under standard smoking conditions. Char samples of the burning cone were obtained from cigarettes which had been extinguished by liquid nitrogen after 9 puffs. Both samples were powdered in mortars. The amount of carbon in the samples was determined by a CHN recorder (Yanaco MT-2type).

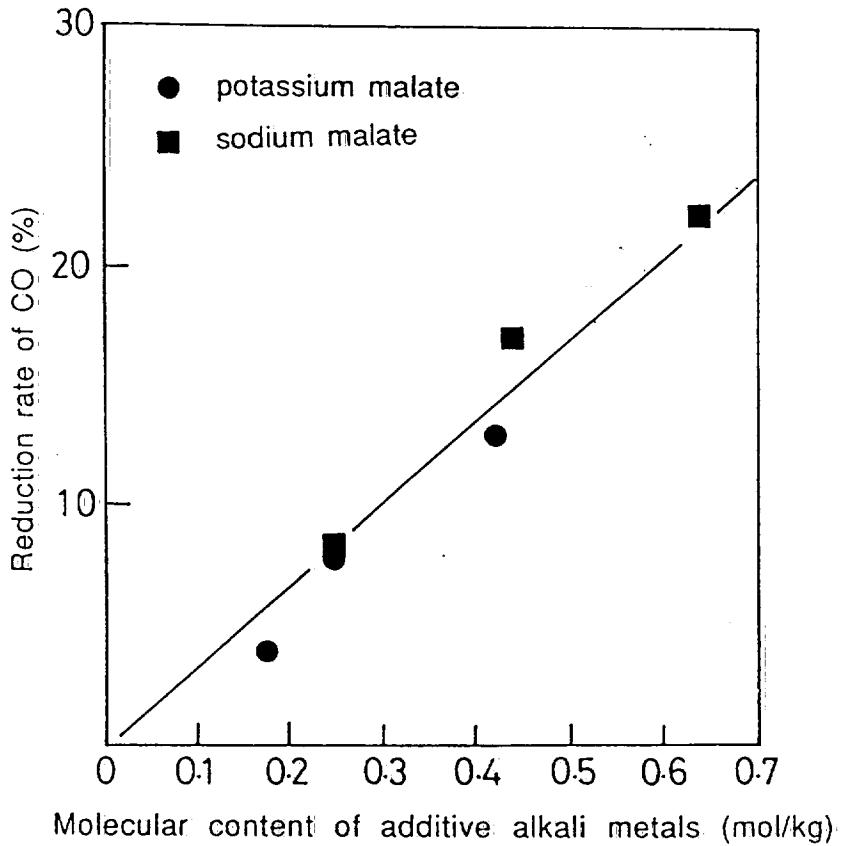
The maximum temperature of the solid phase at the surface of the burning zone during a puff was measured with a scanning infra-red camera interfaced to a digital image processor (Fujitsu INFRA-EYE 5000).

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RESULTS

The effects of the molecular content of additive alkali metals on the reduction rate of CO in the mainstream smoke are shown in Fig. 1. The reduction rate of CO was linearly proportional to the molecular content of additive alkali metals.

FIG. 1
EFFECTS OF MOLECULAR CONTENT OF ALKALI METALS ON REDUCTION RATE OF CARBON MONOXIDE (FRACTIONAL VOLUME 0.32)



DTG curves are shown in Fig. 2. In an atmosphere of nitrogen, the DTG curves were very similar regardless of the additive alkali metals, while in an atmosphere of air, the alkali metal salts affected the DTG curves significantly. As shown in Table 1, the amount of residue at 400°C in air was independent of the additive alkali metal salts. On the other hand, the amount of residue of tobacco with additives at 600°C in air was greater than that of the control tobacco. This indicates that the addition of the alkali metal had an effect on the oxidation of the char.

The DSC curves obtained from Sample A (a mixture of untreated tobacco char and K₂CO₃) were not influenced by the amounts of additives (Fig. 3). On the other hand, the first peak was absent from the DSC curves obtained from Sample B (char made from tobacco treated with potassium malate) (Fig. 4). Therefore, it can be said that the addition of alkali metal salts affected the process of carbonization, but had no direct effect on the oxidation of chars.

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FIG. 2

DTG CURVES OF TOBACCO WITH AND WITHOUT ALKALI METAL SALT ADDITIVES

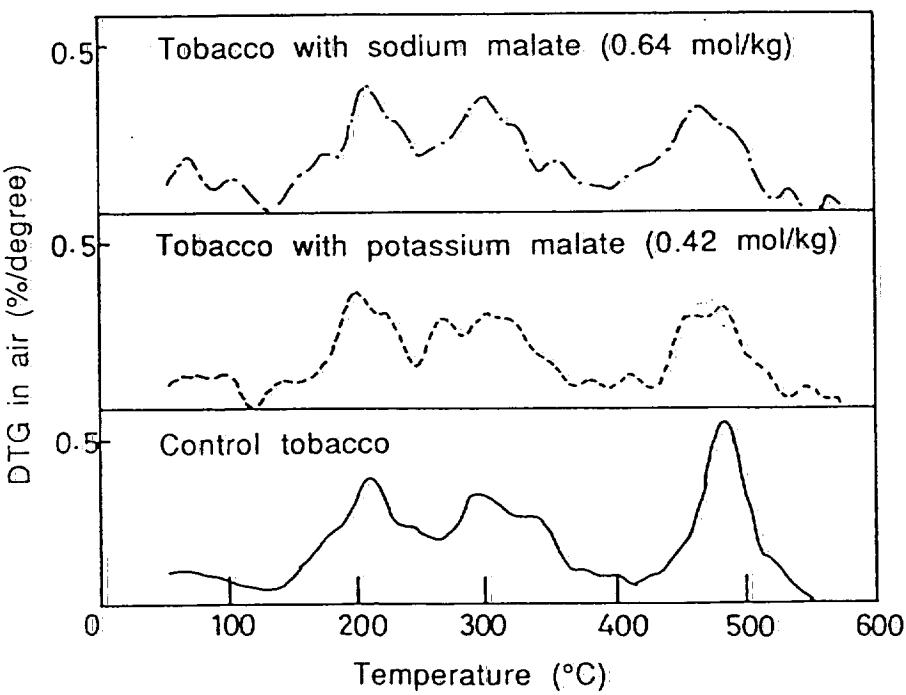
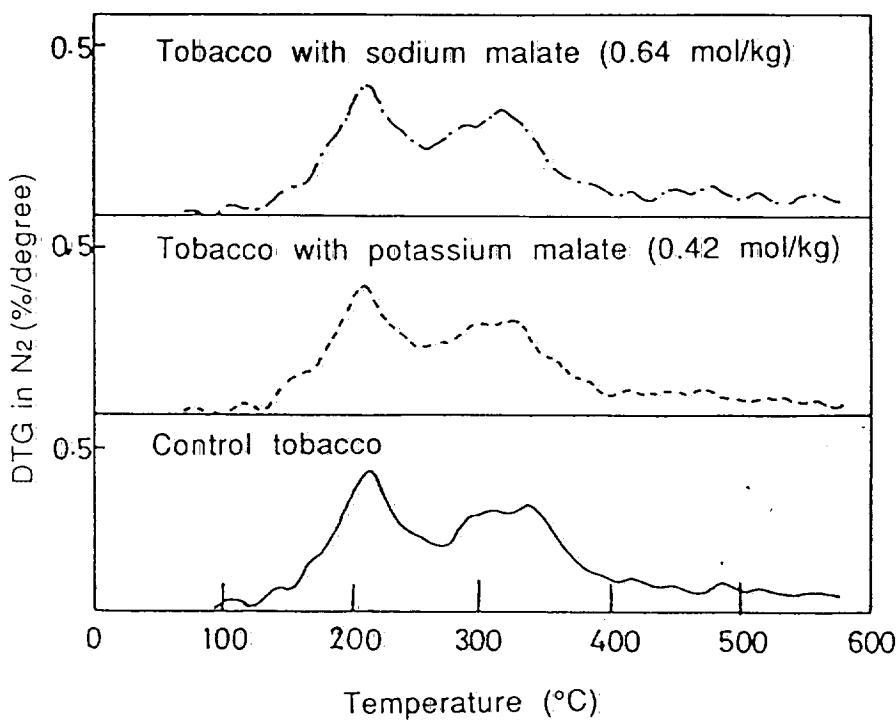
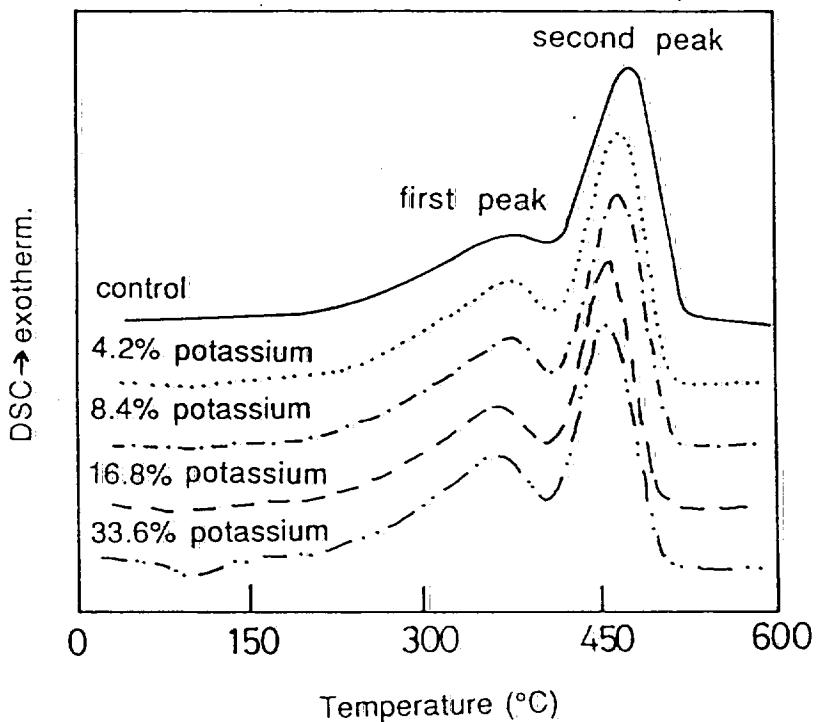


TABLE 1.
THE AMOUNT OF RESIDUE OF TOBACCO WITH AND WITHOUT ALKALI METAL SALTS BY THERMOGRAVIMETRY IN AN ATMOSPHERE OF AIR

Additive	Molecular content mol/kg	Amount of residue at 400°C %	at 600°C %
Control		37.4	8.6
Potassium malate	0.42	38.9	13.4
Sodium malate	0.64	39.3	13.8

FIG. 3
DSC CURVES OF SAMPLE A (MIXTURE OF UNTREATED TOBACCO CHAR AND K₂CO₃)



The surface area of char made from tobacco treated with potassium malate (Sample B) is shown in Fig. 5. The surface area is represented by the amounts of carbonaceous residue without additives. The surface area of chars decreased with increasing potassium content. These results support the idea that potassium in tobacco produces the more stable char during thermal decomposition of the tobacco constituents.

The apparent amount of oxygen consumed during the puff was estimated from the gaseous components in the mainstream smoke. The amount of oxygen consumed by smoking decreased with increasing alkali metals (Table 2). Thus, it can be considered that alkali metals inhibited the combustion of tobacco.

The carbon content of the burning cone was almost constant. However, the carbon content of the ash increased slightly with an increasing amount of alkali metal (Table 2).

FIG. 4
DSC CURVES OF SAMPLE B
(CHAR MADE FROM TOBACCO TREATED WITH POTASSIUM MALATE)

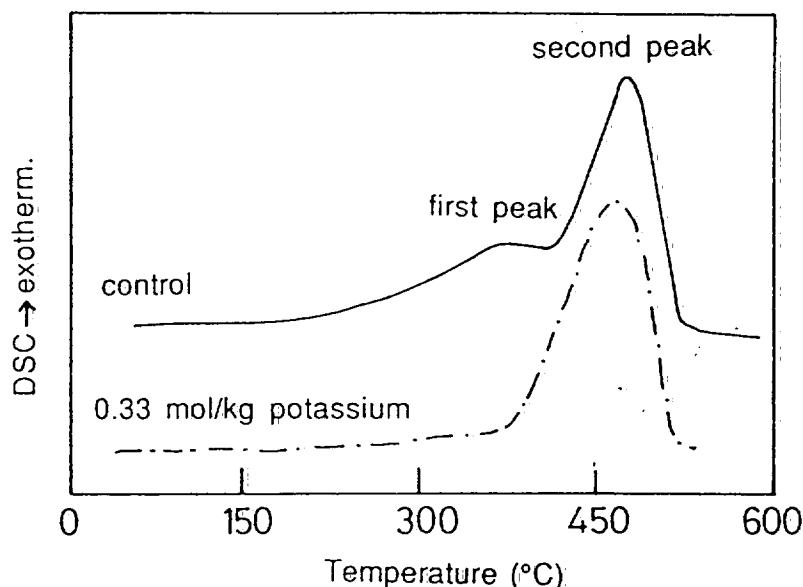
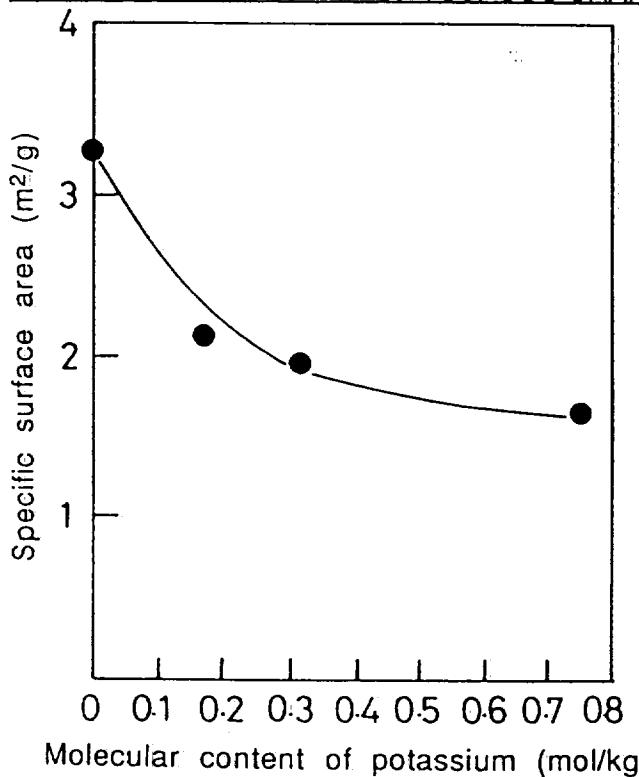


FIG.5
SPECIFIC SURFACE AREA OF TOBACCO CHAR



Yields of char from the extinguished burning cone were estimated from the alkali metal content of the burning cone. The yield of char in the burning cone was about 28% and was independent of the amount of additive alkali metals.

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This tendency was in accordance with the yield of carbonaceous residue obtained from by heating with the electric furnace for the DSC measurement (Table 3).

When alkali metals were added on tobacco, the maximum temperature of solid phase during puffing was lowered (Table 4).

TABLE 2
THE AMOUNT OF OXYGEN CONSUMED DURING PUFFING, THE WEIGHT OF CARBON IN CONE AND ASH, AND YIELDS OF TOBACCO CHAR (FRACTIONAL VOLUME 0.32)

Additive	Molecular content mol/kg	Oxygen consumed ml/cig.	Weight of carbon in cone mg/cone	Weight of carbon in ash mg/cig.	Yield of tobacco char %
Control	0	26.0	8.9	3.2	27.3
Potassium malate	0.18	25.6	9.8	3.4	27.7
	0.25	24.2	9.6	3.7	28.3
	0.42	23.8	9.8	3.8	26.7
Sodium malate	0.25	25.2	9.1	4.6	27.4
	0.44	24.2	8.9	5.9	31.0
	0.64	24.0	8.7	6.3	27.5

TABLE 3
YIELDS OF CHAR (SAMPLE B: CHAR MADE FROM TOBACCO TREATED WITH POTASSIUM MALATE USING AN ELECTRIC FURNACE)

Additive	Molecular content mol/kg	Yields of tobacco char %
Control	-	27.8
Potassium malate	0.18	28.2
	0.33	30.4
	0.76	28.8

TABLE 4
THE MAXIMUM TEMPERATURE OF SOLID PHASE DURING PUFFING (FRACTIONAL VOLUME 0.31)

Cigarette	Additive content mol/kg	Maximum temperature of solid phase °C
Control	-	801 (n=50)
Potassium additive	0.42	781 (n=65)
Sodium additive	0.64	731 (n=34)

DISCUSSION

The DSC curve of tobacco char in air is made up of 2 peaks. Muramatsu *et al.* considered that the first peak of DSC curve is attributable to oxidation of a more reactive portion of the char (5). In the case of cellulosic char with sodium, it is reported that the first peak corresponds to the oxidation of the aliphatic component and the second peak corresponds to the oxidation of the more stable aromatic component.(6). As shown in Figs. 4 and 5 the first peak of the DSC curve disappeared and the surface area decreased in the case of carbonaceous residue of tobacco treated with alkali metal salts. It is obvious that alkali metal salts form a more stable char in the decomposition process of tobacco.

Actually, as shown in Table 2, the amount of oxygen consumed during the puffs decreased, although the yield of the char from the burning cone was independent of the amount of additive alkali metals. Also, the carbon content in the ash, which fell naturally during smoking, increased with increasing amount of alkali metal salts. These results of the measurements of cigarettes corresponded with those of pyrolysis. The more stable char reduces the heat release on combustion. Actually, the temperature of the burning cone was lowered by the addition of alkali metals.

Consequently, alkali metals form a stable char in the decomposition process of tobacco, so that the formation of CO in the combustion decreases. Further, since the more stable char reduces the heat release, the temperature of the burning cone falls, and the formation of CO through carbonaceous reduction is reduced.

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